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(54) DEVELOPER FOR COLORED PHOTSENSITIVE RESIN COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To extremely diminish residue in a non-image area after development and to extremely suppress the peeling of a pattern and the reduction of film thickness by using a specified anionic surfactant.

SOLUTION: This developer for a colored photosensitive resin compsn. is an aq. alkali soln. contg. at least one kind of anionic surfactant which is a polyoxyalkylene deriv. and at least one kind of anionic surfactant having an arom. group as essential components or an aq. alkali soln. contg. at least one kind of anionic surfactant having a long chain alkyl group and an arom. group in each molecule as an essential component. The polyoxyalkylene deriv. is, e.g. a sulfonate, phosphoric ester or phosphoric ester salt. A sulfonate represented by the formula $R-O(CH_2CH_2O)_nSO_3M$ [where R is alkyl

or alkylphenyl, M is a base and (n) is a positive integer] is especially suitable.

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CLAIMS

[Claim(s)]

[Claim 1] (A) The developer for coloring photopolymer constituents characterized by
being the alkali water solution of the anion system surfactant of the anionic surfactant
which is a polyoxyalkylene derivative which has a kind and (B) aromatic series radical
at least which contains a kind at least.

[Claim 2] The developer for coloring photopolymer constituents characterized by being the alkali water solution of the anion system surfactant which has a long-chain alkyl group and an aromatic series radical in a molecule which contains a kind at least.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] In case this invention forms a coloring image with a coloring photopolymer constituent, it relates to a useful developer, especially the developer for coloring photopolymer constituents with which the development nature of the non-image section has been improved.

[0002]

[Description of the Prior Art] Forming a coloring image is performed in manufacture of the color filter used for for example, a liquid crystal display component, a photography component, etc., creation of the KARAPU roofing sheet used by the proof of printing, etc. by performing development after image exposure conventionally using a coloring photopolymer constituent. Manufacture of the color filter used for a liquid crystal display component, a photography component, etc. as one example is explained. Although a color filter forms the pixel and black matrix of the shape of the shape of a mosaic, and a stripe on transparent substrates, such as glass, the so-called following pigment-content powder methods are used as one of the approaches of forming the pixel and black matrix of the shape of the shape of these mosaics, and a stripe. That is, a pigment is first mixed with a photopolymer, a solvent, etc., a coloring photopolymer constituent is prepared, this prepared coloring photopolymer constituent is applied to a substrate through direct or stratum disjunctum, and after exposing the dried coloring photopolymer paint film in the shape of an image after desiccation, a coloring pattern is formed by developing negatives with a developer and removing a fusibility resin part. And the developing-negatives methods, such as immersion development, rocking development, spray development, and paddle development, are taken by the development of the paint film which consists of such a coloring photopolymer constituent.

[0003] However, since the insoluble pigment was used for the developer, the coloring image obtained by the pigment-content powder method had conventionally the problem of producing residue in the non-image section. The approach

(JP,7-120935,A) using the alkaline developer which contains the approach (JP,5-188602,A) using the alkaline developer containing an anion system surfactant and the Nonion system surfactant and the Nonion system surfactant as a developer in order to reduce the residue of such the non-image section etc. is learned, and using the developer which contains an anion system surfactant a vinyl-pyrrolidone system polymer and if needed as a suitable developer for the coloring photopolymer containing the pigment which has an anionic radical is further indicated by JP,5-27451,A.

[0004]

[Problem(s) to be Solved by the Invention] Thus, although various attempts including the approach of adding a surfactant to a developer are made in order to reduce the residue of the non-image section of a coloring photopolymer constituent, the present condition is that reduction of the residue of the non-image section cannot yet say it as sufficient thing depending on the conventional well-known developer including what is depended on the developer containing a surfactant, but still much more improvement is demanded. Therefore, the purpose of this invention is in view of the situation described above to offer the developer for coloring photopolymer constituents very effective in removal of the residue of the non-image section.

[0005]

[Means for Solving the Problem] this invention persons reached [that the residue of the non-image section is effectively removable, and] a header and this invention by using the developer which has the following presentations as a developer for coloring photopolymer constituents, as a result of repeating research wholeheartedly in view of the above-mentioned situation. That is, the developer for coloring photopolymer constituents of this invention is characterized by consisting of an alkali water solution of the anion system surfactant which has a long-chain alkyl group and an aromatic series radical in a molecule which contains a kind at least as an indispensable component as the alkali water solution of the anion system surface activity material of the anionic surfactant which is (A) polyoxyalkylene derivative which has a kind and (B) aromatic series radical at least which contains a kind at least, or an indispensable component.

[0006] The developer for coloring photopolymer constituents which consists of an alkali water solution of the anion system surfactant of the anionic surfactant which is (A) polyoxyalkylene derivative which has a kind and (B) aromatic series radical at least which is one mode of this this invention, and which contains a kind at least first hereafter is explained to a detail. It is the surfactant used and its combination that the

developer concerning the first mode of this invention differs from the well-known developer conventionally. That is, it is in the anion system surfactant which is a polyoxyalkylene derivative, and two kinds of surfactants of the anion system surfactant which has an aromatic series radical being used in the developer of this invention. (A) As an anion system surfactant which is the polyoxyalkylene derivative of a component, a sulfonate, phosphoric ester, phosphate, etc. are raised, for example, and a polyoxyethylene-alkyl-ether sulfonate, a polyoxyethylene-alkyl-phenyl-ether sulfonate, alkyl phenoxy polyoxyethylene PUROPIRUSURUHON acid chloride, a polyoxyethylene propyl sulfonate, a polyoxyethylene styryl phenyl ether sulfonate, etc. are raised.

[0007] Also in these, especially the sulfonate expressed with the following general formula is suitable.

[0008] $R-O(CH_2CH_2O)_nSO_3M$ (however, R an alkyl group or an alkylphenyl radical, and M a base and n positive integer)

In an upper type, the bases of M may be inorganic and organic any, and they are alkali-metal ion, especially Na^+ as an inorganic base. It is desirable. Moreover, as an organic base, organic amines and the fourth class ammonium ion are raised, for example, ammonium ion, alkyl ammonium ion, and permutation alkyl ammonium ion are desirable, and tetramethyl ammonium ion, methyl triethanol ammonium ion, etc. are especially raised as an example.

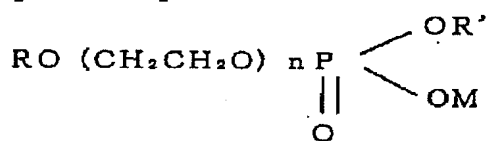
[0009] Specifically as a compound expressed with the above-mentioned general formula, polyoxyethylene lauryl ether sulfonic-acid sodium, polyoxyethylene nonylphenyl ether sulfonic-acid sodium, polyoxyethylene propyl sulfonic-acid sodium, etc. are raised.

[0010] On the other hand, as phosphoric ester and phosphate, polyoxyethylene-alkyl-ether phosphoric ester and its salt, polyoxyethylene-alkyl-aryl-ether phosphoric ester, its salt, etc. are raised among the anion system surface active agents which are the above-mentioned polyoxyalkylene derivatives.

[0011] Also in these, the phosphoric ester shown by the following general formula and its salt are especially desirable.

[0012]

[Formula 1]



[0013] (however, R — an alkyl group or an alkyl aryl radical, and R' — H, M, or R (OCH₂ CH₂) — m and m are zero or more integers, and n and M are the same as the above)

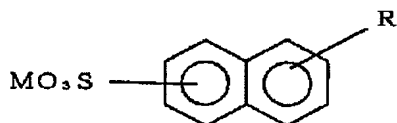
Specifically as a compound expressed with the above-mentioned general formula, polyoxyethylene nonyl ether phosphoric-acid ethyl, polyoxyethylene lauryl ether sodium phosphate, polyoxyethylene octyl phenyl ether sodium phosphate, etc. are raised. The anion system surfactant which are these polyoxyalkylene derivatives may be used independently, and more than one may be mixed and it may be used.

[0014] Furthermore, as an anion system surfactant which has the aromatic series radical of the above-mentioned (B) component, the sulfonate represented with an aryl sulfonate and a permutation aryl sulfonate is raised as a desirable thing. Specifically, they are a naphthalene sulfonate, a permutation naphthalene sulfonate and the formaldehyde condensate of these naphthalene sulfonates, or the formaldehyde condensate of benzenesulfonic acid salts.

[0015] A naphthalene sulfonate, a permutation naphthalene sulfonate, or the formaldehyde condensate of these naphthalene sulfonates is shown by for example, the following general formula.

[0016]

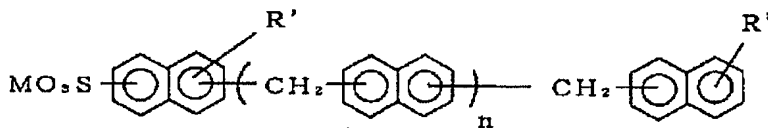
[Formula 2]



[0017] (However, an alkyl group, or H and M of R are the same as that of the above)

[0018]

[Formula 3]



[0019] (However, H, an alkyl group, an alkoxyl group, or OH and n are zero or more integers, and M of R' is the same as that of the above)

Specifically as a compound expressed with the above-mentioned general formula, naphthalene sulfonic-acid sodium, methylnaphthalene sulfonic-acid sodium, a naphthalene sulfonic-acid sodium formaldehyde condensate, etc. are raised. These

may be used independently, or more than one may be combined and they may be used. [0020] By the way, although temporary effectiveness is in removal of the residue of the non-image section even if only one side of them is used for the anion system surfactant which has the aromatic series radical of the anion system surfactant which is the derivative of polyoxyalkylene of the above-mentioned (A) component, or the (B) component, the residue of the non-image section decreases sharply by combining both (A) component and (B) component, and resolution also improves sharply further.

[0021] The anion system surfactant which these operating rates in the inside of an alkali developer are weight ratios, and is the derivative of polyoxyalkylene when using in this invention combining the anion system surfactant which is the derivative of the polyoxyalkylene which is the (A) component, and the anion system surfactant which has the aromatic-series radical which is the (B) component: It is desirable that the anion system surfactants which have an aromatic series radical are 20:1 – 1:50, 10:1–1:20 are more desirable, and 2:1–1:5 are still more desirable. The improvement of the residue of the non-image section does not become sufficient thing, there is little amount of the anion system surfactant used which has an aromatic series radical when there are more rates of the anion system surfactant which is the derivative of polyoxyalkylene than 20:1, although the improvement of the residue of the non-image section is made when the rate of an anion system surfactant of having an aromatic series radical on the contrary exceeds 1:50, exfoliation of the image section may start to coincidence, and it is not desirable.

[0022] Moreover, the concentration of the anion system surfactant which is the derivative of polyoxyalkylene in the developer for coloring photopolymer constituents of this invention is 0.1 – 7 % of the weight still more preferably 0.01 to 10% of the weight preferably 0.001 to 20% of the weight. Moreover, the concentration of the anion system surfactant which has an aromatic series radical is 0.1 – 7 % of the weight still more preferably 0.01 to 10% of the weight preferably 0.001 to 20% of the weight. It is not desirable from an economical standpoint except that the viscosity of a developer may become high too much or exfoliation of the film of the image section may break out, when effectiveness of this invention may be unable to be acquired as such concentration is 0.001 or less % of the weight, and 20 % of the weight is exceeded.

[0023] Moreover, other one mode of the developer for coloring photopolymer constituents of this invention is an alkali water solution which contains the anion system surfactant which has a long-chain alkyl group and an aromatic series radical in a molecule as an indispensable component. Although the anion system surfactant which has this long-chain alkyl group and an aromatic series radical in a molecule may

be used with the anion system surfactant which is the derivative of the above-mentioned polyoxyalkylene, or the anion system surfactant which has an aromatic series radical, effectiveness is in removal of the above-mentioned fogging, and improvement in resolution also by using independently.

[0024] Alkylbenzene sulfonates, alkyl naphthalenesulfonate, etc. are raised as an example of the anion system surface active agent which has this long-chain alkyl group and an aromatic series radical in a molecule. As a concrete compound, sodium dodecylbenzenesulfonate, DESHIRU diphenyl ether disulfon acid sodium, DESHIRU naphthalene sulfonic-acid sodium, etc. are raised.

[0025] And when using into a developer the anion system surfactant which has this long-chain alkyl group and an aromatic series radical in a molecule, that concentration has 0.1 – 20 desirable % of the weight, its 0.3 – 10 % of the weight is more desirable, and its further 0.4 – 5 % of the weight is more desirable. When it was 0.1 or less % of the weight, and removal of the residue of the non-image section is not fully performed and 20 % of the weight is exceeded, while the viscosity of a developer becomes high, exfoliation of the image section may arise and it is not desirable from an economical viewpoint.

[0026] In this invention, although fogging of the non-image section decreases sharply and resolution improves further combining the anion system surfactant which is a polyoxyalkylene derivative, and the anion system surfactant which has an aromatic series radical, or by using the anion system surfactant which has a long-chain alkyl group and an aromatic series radical in a molecule, the reason is not clear.

[0027] However, according to the old knowledge, various things are originally known as a pigment, but The pigment used especially on the occasion of manufacture of a color filter Typically Blue pigments, such as red pigments, such as an anthraquinone system and the Quinacridone system, and a phthalocyanine system, And the thing which toned these pigments with purple pigments, such as yellow pigments, such as a JISUAZO system, and a dioxazine system, etc., It is a carbon black independent or the thing which added pigments, such as red, blue, green, yellow, and purple, further, and, generally these pigments include many aromatic series rings, hetero aromatic series rings, unsaturated bonds, etc. in the molecular structure. Since the anion system surfactant which has the above-mentioned aromatic series radical has high compatibility with a pigment-content child's aromatic series ring, a hetero aromatic series ring, and an unsaturated bond, it is thought effectively that the paint film of the non-image section containing a pigment is removable. However, if the anion system surfactant which has an aromatic series radical is added so much, exfoliation of the

image section will also be started to coincidence.

[0028] The anion system surfactant which is a polyoxyalkylene derivative on the other hand is combining the anion system surfactant which is this polyoxyalkylene derivative, although what is promoting permeation to the pigment paint film of a developer is presumed, and is effectively considered that the anion system surfactant which has an aromatic series radical can remove residue of the non-image section, without low concentration also exfoliating the image section.

[0029] Moreover, it is thought that effectiveness is in the molecular structure with the anion system surfactant possessing an alkyl group and an aromatic series radical even if it uses independently since the both sides of the affinity effectiveness of the surfactant to an above-mentioned pigment and the permeation effectiveness to the paint film of a developer are provided.

[0030] In addition, although using it combining the polyoxyalkylene which are an anion system surfactant and the Nonion system surfactant conventionally was known, as shown by the example of a comparison, compared with this invention, it was not effective in removal of the residue of the non-image section, and improvement in resolution. As this reason, originally, the above-mentioned Nonion system surfactant has an anion system surfactant and bad compatibility, and is presumed to be that on which the Nonion system and an anion system surfactant act independently, respectively for this reason. On the other hand, in order for this invention to be combining the anion system surfactant which introduced the anionic functional group into the Nonion system surfactant of a polyoxyalkylene series, and for its compatibility of the surfactant with which two kinds of molecular structures differ from an operation to improve and to act in collaboration, the residue of the non-image section decreases sharply and it is thought that resolution improves. In addition, this explanation is for considering as an aid of an understanding of this invention, and does not limit this invention.

[0031] On the other hand, the alkali used in the developer for coloring photopolymer constituents of this invention You may be which alkaline compound. inorganic or organic -- as an inorganic alkalinity compound Alkali metal, alkaline earth metal, or the hydroxide of ammonium, A silicate, a metasilicate, phosphoric-acid hydrogen salt, ammonia, etc. specifically A sodium hydroxide, A potassium hydroxide, a sodium silicate, a potassium silicate, a sodium carbonate, potassium carbonate, phosphoric-acid 3 sodium, phosphoric-acid 3 potassium, etc. again as an organic alkalinity compound Organic amines, a hydroxylation quaternary ammonium base, etc. specifically Monochrome, JI or a trimethylamine, monochrome, JI, or triethylamine,

Monochrome or diisopropylamine, monochrome, JI or triethanolamine, monochrome, JI or tri-isopropanolamine, ethyleneimine, ethylene diimine, tetramethylammonium hydroxide, a choline, etc. are raised. These alkali may be independent or may be used combining two or more sorts. In addition, as alkali which does not contain a metal ion, the thing of a publication can also be used, for example for a U.S. Pat. No. 4,729,941 specification. And as for the developer of this invention, it is desirable to have 8.5 or more pH.

[0032] In case physical force, such as rocking development, spray development, and paddle development, is applied and developed, in order to remove residue more effectively, a water-soluble polymer may be further included in this developer. As an example of a water-soluble polymer, polyvinyl alcohol, polyacrylic acid, polymethacrylic acid, a polyvinyl pyrrolidone, etc. can be raised.

[0033] Moreover, the developer of this invention may contain the defoaming agent further. As a defoaming agent, various well-known things, such as a silicone system, a higher-alcohol system, and an ester system, can be used.

[0034] Moreover, the developer of this invention is supplied to a user, after the developer has condensed, and it also contains the so-called concentration type which is diluted and is used at the time of use of developer.

[0035] As long as the coloring photopolymer constituent with which the developer of this invention is applied is a photopolymer constituent well-known alkali development type [colored] to the former which changes the solvent dissolution property of a constituent by the exposure of ultraviolet rays, an X-ray, an electron ray, etc. including pigments, such as a color, an organic pigment, an inorganic pigment, carbon black, and a silica, which thing is sufficient as it. As such a photopolymer constituent, the thing [constituent / which consists of the constituent of an azide system sensitization agent and FE Norian novolak resin, a polyfunctional monomer like trimethylopropane triacrylate and an alkali fusibility binder, and a photopolymerization initiator] using quinone diazide system sensitization agents, such as o-quinone diazide, as a thing of POJITAIPU is raised with the thing of NEGATAIPU as an example again. These coloring photopolymer constituent is applied to a base material or substrates, such as glass and plastic film, through direct or stratum disjunctum according to the purpose of use.

[0036] In addition, it cannot be overemphasized that it is applicable also to the photopolymer constituent in which development is possible with the alkaline water solution or water of this invention with which the developer is not colored.

[0037]

[Example] Hereafter, this invention is further explained to a detail using an example. In addition, this invention is not limited to this example.

[0038] The developer used in an example and the example of a comparison is shown in Table 1.

[0039]

[Table 1]

表 1

番号	現像液の組成	
現像液1	水酸化テトラメチルアンモニウム ポリオキシエチレンラウリルエーテルスルホン酸ナトリウム ナフタレンスルホン酸ナトリウム	0.15N 1% 3%
現像液2	水酸化テトラメチルアンモニウム ポリオキシエチレンラウリルエーテルスルホン酸ナトリウム デシルジフェニルエーテルジスルホン酸ナトリウム	0.15N 1% 1%
現像液3	水酸化カリウム ポリオキシエチレンラウリルエーテルスルホン酸ナトリウム ナフタレンスルホン酸ナトリウム	0.06N 1% 3%
現像液4	水酸化カリウム ドデシルベンゼンスルホン酸ナトリウム	0.06N 1%
現像液5	水酸化テトラメチルアンモニウム デシルジフェニルエーテルジスルホン酸ナトリウム	0.15N 3%
現像液6	水酸化テトラメチルアンモニウム	0.15N
現像液7	水酸化テトラメチルアンモニウム ポリオキシエチレンラウリルエーテル ナフタレンスルホン酸ナトリウム	0.15N 1% 3%
現像液8	水酸化テトラメチルアンモニウム ナフタレンスルホン酸ナトリウム	0.15N 4%

(表中、Nは規定、%は重量%である)

[0040] On the other hand, the following sample was created as a coloring photopolymer constituent.

[0041]

Preparation (1) coloring photopolymer constituent 1 of a photopolymer constituent:
Polyhydroxy styrene (average molecular weight about 20,000) 40g 4 and 4-diazo

stilbene -2, 2-disulfon acid-N, and N- 15g Diethylene oxy-ethyl amide Hexamethoxy methyl melamine 6g Carbon black dispersion liquid containing a dispersant (pigment content 17 % of the weight) The constituent which the above-mentioned nonsolvent component contains 20% of the weight was adjusted using propylene glycol methyl ether acetate as a 180g solvent.

[0042] (2) Coloring photopolymer constituent 2 : it prepared like the coloring photopolymer constituent 1 among each component of said coloring photopolymer constituent 1 except having used the red pigments (C. I. pigment red 177) containing dispersion liquid, a blue pigment (C. I. pigment blue 15:6), green pigments (C. I. pigment Green 36), and 180g (17 % of the weight of pigment contents) of these weight mixing dispersion liquid of carbon black instead of carbon black dispersion liquid.

[0043] Spin spreading of said coloring photopolymer constituents 1 and 2 was carried out on the glass substrate at about 1 micrometer of thickness using the transparence substrate for color filter manufacture washed example 1, respectively. Subsequently, it was made to dry for 1 minute at 100 degrees C on a hot plate. The dried coloring photopolymer layer was exposed with the high pressure mercury vapor lamp through the mask of a predetermined configuration. Subsequently, the coloring photopolymer layer which carried out pattern exposure was developed with the phenomenon liquid 1 which has the presentation of Table 1, and the coloring pattern was obtained. When the pattern obtained after development was observed under the microscope, the residue of the non-image section was not accepted in which coloring photopolymer constituent, but the pattern which has a sharp edge was obtained.

[0044] Except having used the developer 2 instead of the developer 1 in example 2 example 1, negatives were exposed and developed like the example 1 and the coloring pattern was obtained. When the pattern obtained after development was observed under the microscope, the residue of the non-image section was not accepted in which coloring photopolymer constituent, but the pattern which has a sharp edge was obtained.

[0045] Except having used the developer 3 instead of the developer 1 in example 3 example 1, negatives were exposed and developed like the example 1 and the coloring pattern was obtained. When the pattern obtained after development was observed under the microscope, the residue of the non-image section was not accepted in which coloring photopolymer constituent, but the pattern which has a sharp edge was obtained.

[0046] Except having used the developer 4 instead of the developer 1 in example 4 example 1, negatives were exposed and developed like the example 1 and the coloring

pattern was obtained. When the pattern obtained after development was observed under the microscope, the residue of the non-image section was not accepted in which coloring photopolymer constituent, but the pattern which has a sharp edge was obtained.

[0047] Except having used the developer 5 instead of the developer 1 in example 5 example 1, negatives were exposed and developed like the example 1 and the coloring pattern was obtained. When the pattern obtained after development was observed under the microscope, the residue of the non-image section was not accepted in which coloring photopolymer constituent, but the pattern which has a sharp edge was obtained.

[0048] Negatives were exposed and developed like the example 1 except having used the developer 6 instead of the developer 1 in example of comparison 1 example 1. When the pattern obtained after development was observed under the microscope, the residue of the non-image section was accepted also in which coloring photopolymer constituent.

[0049] Negatives were exposed and developed like the example 1 except having used the developer 7 instead of the developer 1 in example of comparison 2 example 1. When the pattern obtained after development was observed under the microscope, also in which coloring photopolymer constituent, the residue of the non-image section and peeling of a pattern were accepted.

[0050] Negatives were exposed and developed like the example 1 except having used the developer 8 instead of the developer 1 in example of comparison 3 example 1. When the pattern obtained after development was observed under the microscope, also in which coloring photopolymer constituent, the residue of the non-image section and peeling of a pattern were accepted. Moreover, ***** was also accepted.

[0051] From the above example and example of a comparison, the following thing becomes clear.

(1) If examples 1-5 are compared with the example 1 of a comparison, the developer of this invention is very effective in removal of the residue of the non-image section, and it is clear that the pattern which has a sharp edge is obtained.

[0052] (2) The developer of this invention which combined the polyoxyalkylene series anion system surfactant and the anion system surfactant which has an aromatic series radical when examples 1-3 were compared with the examples 2 and 3 of a comparison of peeling of residue and a pattern and ***** not being in the non-image section, and a good pattern being obtained rather than the developer 8 which used independently the anion system surfactant which has the developer 7 and aromatic

series radical which combined the Nonion system surfactant of a polyoxyalkylene series and the anion system surfactant which has an aromatic series radical, is clear. [0053] (3) A good pattern [be / in the non-image section / peeling of residue and a pattern and film Berry] is similarly obtained for what used independently the surfactant which has an aromatic series ring and an alkyl chain instead of combining a polyoxyalkylene series anion system surfactant and the anion system surfactant which has an aromatic series radical so that clearly from examples 4 and 5.

[0054]

[Effect of the Invention] This invention has the effectiveness that the residue of the non-image section after development, peeling of a pattern, and film Berry can be reduced remarkably, by using the developer which is the developer which is an alkali water solution including the both sides of an anion system surfactant which have the anion system surfactant and aromatic series radical which are a polyoxyalkylene derivative as a developer for coloring photopolymer constituents, or an alkali water solution containing the surfactant which has a long-chain alkyl group and an aromatic series radical in a molecule.

[0055] Moreover, by using the developer of this invention in the production process of a color filter, it is effective in the ability to form the filter layer which has the sharp pixel and the predetermined thickness which the defect by the residue of the non-image section, peeling of a pattern, and film Berry decreases, therefore do not have the defect of color muddiness and a pixel, and the utility value on color filter manufacture is very large.

[Translation done.]